THE EFFECT OF AIR OXIDATION ON SEQUENTIAL SOLVENT EXTRACTION OF THE
ARGONNE PREMIUM COAL SAMPLES

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INTRODUCTION

Sequential solvent extraction of coal with a series of increasingly better solvents (Toluene, THF, DMF, Pyridine) has been used to examine the effect of artificial weathering on several Illinois coals.[1] A similar method with a different set of solvents was recently employed by Kister, et al. on a low-rank French coal.[2] In both cases, each extract is soluble in all later solvents and analysis of the entire set of extracts produces more information than extraction with a single solvent. Because extracts so isolated have experienced some fractionation and concentration, FT-IR and GPC analyses of the extracts often reveal subtle changes due to chemical treatment, such as weathering, not obvious from analysis of the whole coals.

The availability of premium coals is an opportunity for many laboratories to study the effects of both coal rank and coal weathering on a variety of properties of the same coals. Changes in sequential solvent extraction, FT-IR spectra of extracts and residues, GPC analyses of extracts, and solvent swelling of residues brought about by weathering of five Argonne Premium Coals are the subject of this paper.

EXPERIMENTAL PROCEDURES

Argonne Premium coal samples were dried to constant weight in an Abderhalden apparatus at 100°C and 0.05 Torr (standard conditions) immediately prior to extraction or oxidation. Samples were oxidized as thin layers, in recrystallizing dishes covered to exclude dust, but permit free circulation of air, at ambient temperature and humidity for at least four months. Weathering coals were stirred once a week to promote uniform air exposure and redried to constant weight before extraction. Sequential solvent extraction of coals in the order: toluene, THF, DMF, pyridine followed the method described previously.[1] Samples of coal and oxidized coal (7-10 g) were exhaustively extracted with purified, Argon purged, solvents in a Soxhlet apparatus, under an Argon atmosphere. Extraction with each solvent was continued until no color was visible in the siphoning solvent for at least ten hours. All extracts and washing solvents were filtered through 0.45 um Nylon membrane filters before vacuum evaporation and standard drying to constant weight. Residues plus DMF and pyridine extracts were washed several times with 80% methanol/water to remove those solvents.

Gel Permeation Chromatography (GPC) analyses of all extracts were determined on pyridine solutions (6mg/mL) using a train of three Ultragel columns with pyridine mobile phase.[1] KBr pellets (3.0 mg sample/300 mg KBr) were prepared in an nitrogen flushed glove bag and dried under standard conditions to reduce surface moisture. FT-IR spectra were collected at 2 cm^{-1} resolution on a Nicolet 20-DXB spectrometer. Phenol contents were determined by the Blom acetylation procedure[3] with N,N-dimethylaminopyridine (DMAP) as a catalyst. Volumetric solvent swelling of residues with dry, distilled solvents followed standard methods.[4]

RESULTS AND DISCUSSION

Analytical data for coals, oxidized coals, and two residues are presented in Table 1. Preliminary elemental analyses of the coals are based on many analyses by

several labs, the values for the oxidized coals are from single samples. The well-known problems of comparing such data sets are illustrated by the %C values for fresh and oxidized samples of coals 1, 3, and 4. The expected decrease in carbon content with oxidation is not shown. Additional analyses of both sample sets are needed. Volumetric solvent swelling ratios of extraction residues are listed with the coals they were derived from in Table 1. The effect of oxidation on solvent swelling is both rank and solvent dependent. A decrease in swelling correlates with an increase in cross-linking, either from covalent or hydrogen bonds. Swelling of fresh coals increases and then decreases with rank, as does the extractability reported in Table 2. Total extract yield does not correlate directly with swelling in any single solvent, but swelling ability of the solvent is clearly important in determining extract yield. Differences in swelling between toluene and anhydrous ethanol correlate with oxygen contents of the original coals, showing that ethanol is an hydrogen bond donor in swelling experiments. Except for coal #1, changes in toluene and ethanol swelling caused by oxidation correlate with the change in total extract-ability and show that room temperature oxidation can cause either a net increase or decrease in cross-linking depending on the rank of the coal.

Phenol contents of fresh coals generally increased with weathering. Liotta(5), using alkylation with NMR and FT-IR spectroscopy to measure phenols, found the phenol content of a Monterey Illinois 6 coal to be close to our result for Argonne #3, but observed no change upon weathering for several months, in contrast to the increases we measured for the coals in Table 1. This may reflect differences between coals or oxidation procedures or it may indicate that the Blom acetylation procedure is count-ing as phenol other reactive groups in coals through transesterification or anhydride formation. This would cause oxidized coals, which contain esters or acids, to give high phenol analyses. Residues of our oxidized coals usually have fewer phenols than residues of fresh coals.

Sequential solvent extractions are tabulated in Table 2 and summarized in Figure 1. Variations in total yield with rank are consistent with early work by Dryden.(6) In this and previous studies(1), we have shown that total extract yields are reprodu-cible to within $\pm$ 0.5%; that changing the order of extraction to pyridine, toluene, THF, DMF does not change the total extract yield; and that pyridine removes over 97% of all soluble material when it is the first solvent in the sequence. In single solvent extractions with THF or DMF on several Illinois coals, yields equal the sum of the sequential extraction yields for all solvents up through that solvent in the sequence. We believe that each solvent in the sequence can dissolve everything removed by previous solvents plus additional material made soluble by the increased swelling and solvating power of that solvent.

Extracts and residues which have been in contact with DMF or pyridine were washed with 80% methanol/water to remove these solvents. Only for the sub-bituminous coal did the methanol washes extract highly colored material and leave a significant residue (> 0.1%) after evaporation. Small amounts of colloidal material were iso-lated from the membrane filtration of extracts from oxidized #2 and #3 coals. For material balance purposes, methanol solubles were counted as part of total (but not individual) extracts and colloids as part of residues.

On Figure 1, total extract yields for oxidized coals have been plotted at the carbon values of the fresh coals for comparison. Individual solvent extract yields for fresh coals have been plotted on the same graph to illustrate the variation with rank for each solvent in the sequence. Studies which use single solvent extractabil-ity with 'early' solvents such as THF to measure the extent of some reaction within coal risk missing production or loss of material which may be of a size and polarity to dissolve in that solvent but which remains trapped in the coal pores because of the poor swelling characteristics of the solvent.

Of particular note is the unusual pattern of individual solvent extract yields

of coal #1 in contrast to the 'normal'(6) total extract yield for a coal of this rank. This may be due to the low swelling of this coal in the early solvents. Only with the effective swelling solvents, DMF and pyridine, can the potentially soluble material diffuse out of the coal network. FT-IR spectra of extracts (below) support this view. DMF extraction of coal #1 took nearly a month to reach completion because of slow diffusion of extracts from the coal. In general, extraction time correlated with extract yield and solvent viscosity. DMF extractions were always the slowest.

Only the two lowest rank coals showed significant changes in total extract yield after artificial weathering. Previous results with a variety of Illinois coals(1,5) and Bruceton (hvAb) coal(7) led us to expect reduction in extract yield to be more general than observed. Larsen(7) found a significant decrease in pyridine extractability when Bruceton coal was heated at $80^{\circ}C$, in contrast to our results for coal #4. If the different results are due to oxidation temperature, the reactions leading to a decrease in extractability apparently have large free energies of activation. Larsen's values for pyridine solvent swelling of the Bruceton coal showed little change upon oxidation and fall between our values for fresh and oxidized coal #4 (Table 1).

Changes in FT-IR spectra of sequential extracts upon oxidation were much more striking than changes in the spectra of whole coals or insoluble residues, consistent with the idea that sequential solvent extraction fractionates and concentrates mobile material from coal. Smaller, mobile molecules are more reactive and change more upon weathering than the insoluble network. Figures 2 and 3 present FT-IR spectra of the toluene and pyridine sequential extracts from coal #1 (B), oxidized coal #1 (A), and the difference (A-B). The new carbonyl peak at 1722 cm^{-1} is barely visible in the difference spectrum of #1-OX - #1 coal. This new band has been observed previously in oxidized coals and is suggested to be due esters.(8) It is observed in several sequential extracts of coals 1-OX, 2-OX, 3-OX, 4-OX, and 5-OX in this study and is always accompanied by bands near 1260 and 1102 cm^{-1}, consistent with ester formation. The 1722, 1260, and 1102 cm^{-1} bands are more prominent in extracts of higher rank coals. They are small, but visible, in the THF and pyridine extracts of coals 2-OX and 3-OX. That they occur at all in pyridine extracts, produced from coal exhaustively extracted by toluene, THF, and DMF, is consistent with the idea that the superior swelling ability of pyridine is allowing material similar to the toluene extracts to escape.

The difference spectrum of 3-OX (Figure 4) is dominated by a band at 1666 cm^{-1}, which is also present at low intensity in polar extracts of 1-OX, 2-OX, and 5-OX, and possibly as a shoulder in 1-OX, Figure 3. This band was ascribed by previous workers to quinone or related aryl carbonyl functional groups.(8a,9) Many spectra of oxidized coals and their extracts show a single, sharp band at 750 - 725 cm^{-1}. Aromatic C-H bending and mineral matter both produce sharp bands in this region, however these extracts contain less than 2% ash. The source of this band is currently under investigation and, if not an artifact, could serve as a simple marker for weathering.

GPC analyses of the extracts are consistent with Dryden's early observation that molecular size generally correlates with extract yield.(6) Figures 5 - 7 present Molecular Size Profiles of coals #1, #1-OX, and #2. In each profile, GPC traces of all sequential extracts from a coal are plotted together. Profiles for several Illinois coals similar to #3 and #3-OX have been published previously.(1) Comparison of Figure 5 with 6 shows that even though total extract yield was little changed by weathering, a larger fraction is being removed by DMF and this material came from the pyridine extract. Changes in the shapes of the GPC curves indicate that toluene is extracting a broader range of molecular sizes after weathering and that the THF extract of #1-OX contains more oxygenated molecules than the other fractions. GPC curve height is very sensitive to the presence of hydroxyl and carbonyl functional groups.(10) Comparison of Figure 5 with 7 illustrates changes due to rank in both average molecular size and distribution of extracts.

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Table 1   Analyses of Samples (DAF)

Argonne Sample	%C	%H	%N	%S	%O	% Ash	Solvent Swelling in Toluene	Ethanol	Pyridine
#2[a]	74	5.1	—	0.5	19	8	1.31	1.43	1.68
2-OX[b]	70.68	5.77	0.75	0.28	22.60	10.16	1.61	1.52	1.82
#3	77	5.7	—	5.4	10	16	1.64	1.82	2.31
3-OX	78.09	5.99	1.39	5.52	9.01	16.90	1.51	1.53	2.51
3-Res[c]	76.71	5.84	1.68	6.85	8.92	19.91			
3-OX-Res[c]	76.89	5.55	2.32	6.24	9.00	18.85			
#4	83	5.8	—	1.6	8	9	1.54	1.74	2.76
4-OX	83.31	5.91	1.39	2.26	7.13	10.06	1.56	1.63	2.23
#1	87	5.5	—	2.8	4	13	1.17	1.05	1.31
1-OX	87.29	5.37	1.53	3.00	2.81	11.23	1.59	1.37	1.75
#5	91	4.7	—	0.9	3	5	1.06	1.11	1.10
5-OX	89.72	4.95	1.17	0.21	3.95	4.22	1.02	1.05	1.06

a   Preliminary elemental analyses, Dr. Karl Vorres, A N L.
b   Air oxidation, ambient temperature and humidity, four months. Elemental analyses for oxidized coals and residues by Galbraith Laboratories, Knoxville, TN. Ash determined by L.C. Warfel, ASTM D 3174.
c   Insoluble residue from sequential extraction (Table 2).

Table 2   Sequential Solvent Extraction Yields
Weight %

Argonne Sample	Toluene Extract	THF Extract	DMF Extract	Py Extract	Total Extract	Insoluble Residue	Material Balance
#2	2.16	1.38	1.76	0.34	6.1[a]	91.8	97.9
2-OX	2.35	0.97	3.52[b]	0.54	9.0[c]	86.9	95.9
#3[d]	7.08	7.76	11.40	0.86	27.1	75.5	102.6
3-OX	5.18	5.08	7.38	0.54	18.2	84.8	103.0
#4	5.80	8.18	10.35	0.64	25.0	76.0	101.0
4-OX	5.72	7.78	10.97	1.18	25.6	73.7	99.3
#1[d]	0.58	0.16	12.63	7.56	20.9	77.9	98.8
1-OX	1.12	0.19	17.37	1.45	20.1	76.3	96.4
#5	0.40	0.24	0.25	0.30	1.2	100.2	101.4
5-OX	0.37	0.37	0.48	0.28	1.5	96.3	97.8

a   Includes 0.44% material recovered from the MeOH/H$_2$O wash of the residue.
b   An additional 1.20% was recovered from the MeOH/H$_2$O wash of the extract.
c   Includes 0.37% material recovered from the MeOH/H$_2$O wash of the residue.
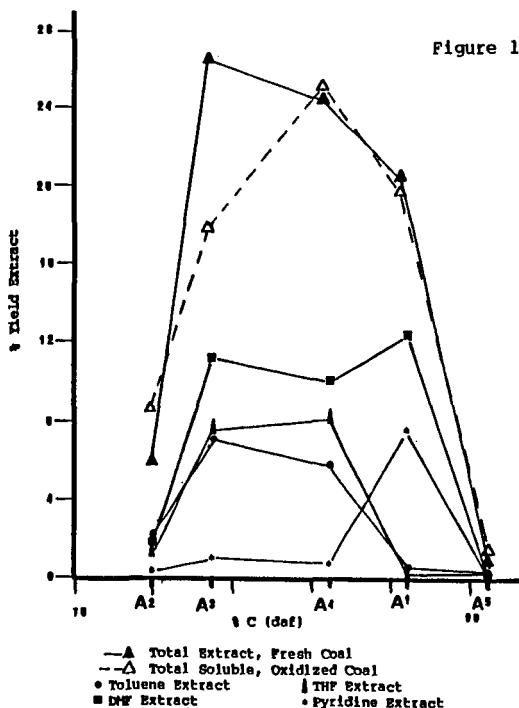d   Average of duplicate extractions.

Figure 1   Extraction yield as a function of rank (% C) for Argonne Premium Coals A$_1$-A$_5$.

—▲ Total Extract, Fresh Coal
--△ Total Soluble, Oxidized Coal
● Toluene Extract   ▲ THF Extract
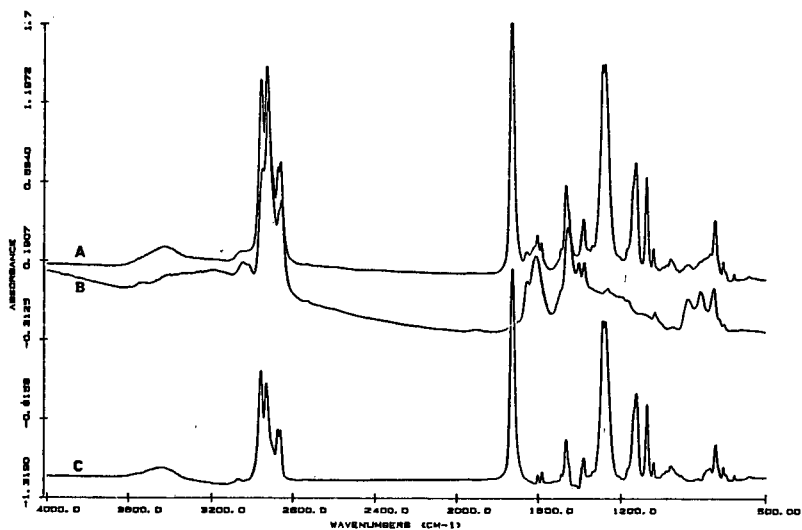■ DMF Extract   ◆ Pyridine Extract

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Figure 2   FT-IR spectra of toluene extracts from Argonne #1.
            A) Oxidized coal, B) Fresh coal, C) Difference A-B.
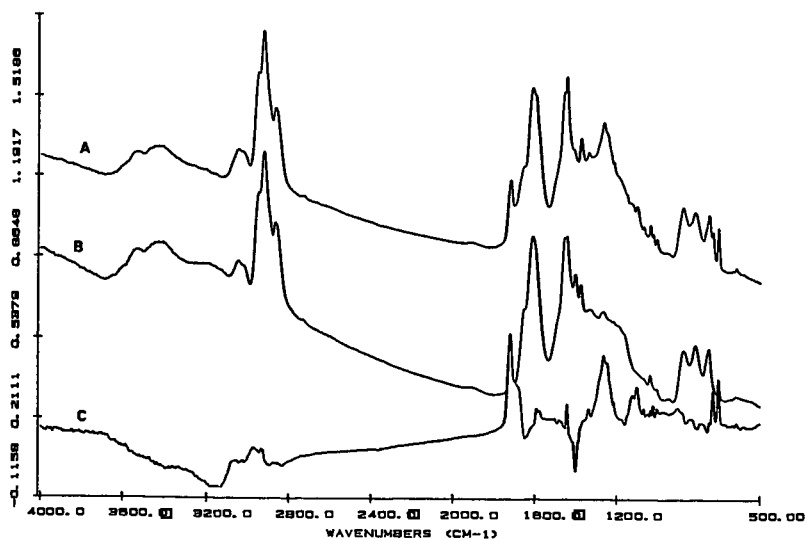

Figure 3   FT-IR spectra of pyridine extracts from Argonne #1.
            A) Oxidized coal, B) Fresh coal, C) Difference A-B.   298
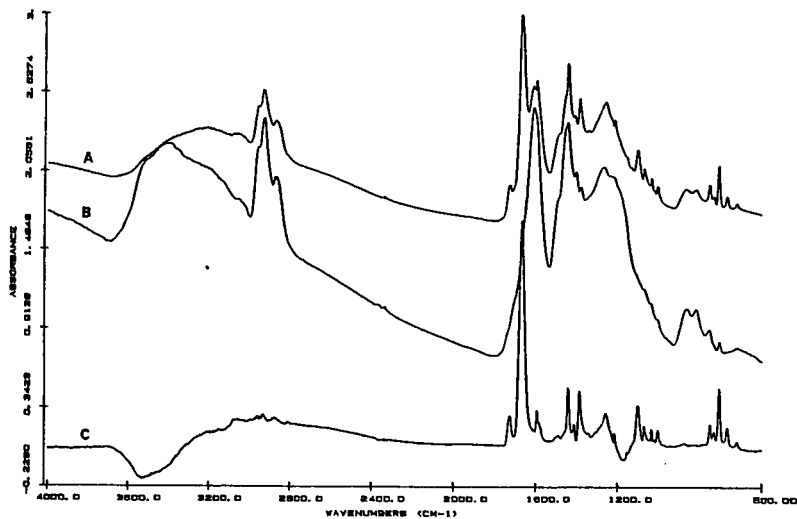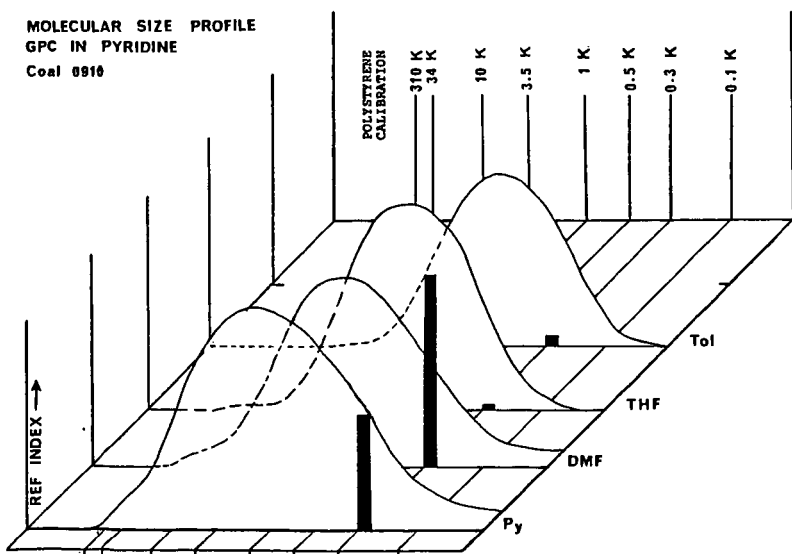
Figure 4   FT-IR spectra of pyridine extracts from Argonne #3.
            A) Oxidized coal, B) Fresh coal, C) Difference A-B.

Figure 5   GPC traces from Argonne #1. Vertical bars indicate fraction
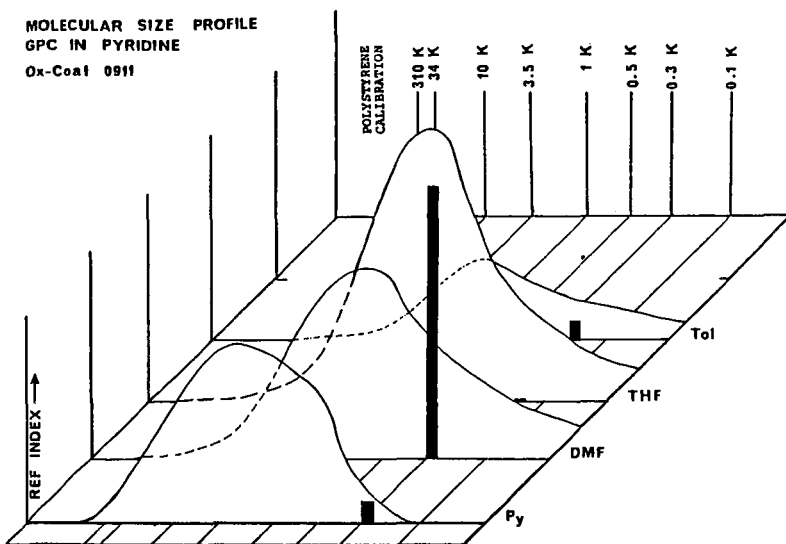   of total extract removed by indicated solvent.

MOLECULAR SIZE PROFILE
GPC IN PYRIDINE
Ox-Coal 0911

POLYSTYRENE CALIBRATION
310 K 34 K 10 K 3.5 K 1 K 0.5 K 0.3 K 0.1 K

REF INDEX →

Tol
THF
DMF
Py

Figure 6   GPC traces from Argonne #1-OX. Vertical bars indicate fraction of total extract removed by indicated solvent.

MOLECULAR SIZE PROFILE
GPC IN PYRIDINE
Coal 0920

POLYSTYRENE CALIBRATION
310 K 34 K 10 K 3.5 K 1 K 0.5 K 0.3 K 0.1 K
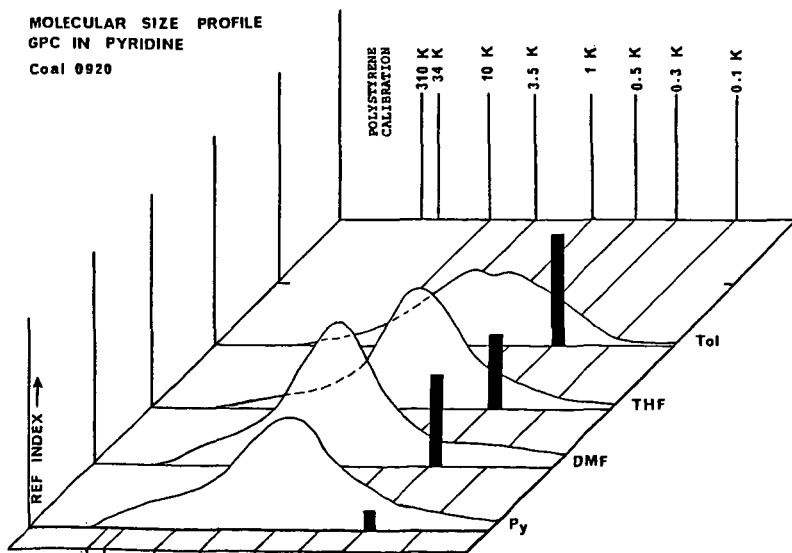
REF INDEX →

Tol
THF
DMF
Py

Figure 7   GPC traces from Argonne #2. Vertical bars indicate fraction of total extract removed by indicated solvent.

300